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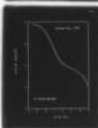MAY 77 M SHEN, D SOONG, D R HANSEN N00014-75-C-0955

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VISCOELASTIC PROPERTIES OF HOMOGENEOUS

BLOCK POLYMERS

by

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May 15, 1977

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INTRODUCTION

It is well known that most block copolymers show microphase separation as a consequence of their positive free energy of mixing between the polymeric blocks[1]. These heterophase polymers have been found to exhibit many unique properties that are dramatically different from those of the homogeneous polymers[2]. However, a limited number of block copolymers have shown no microphase separation, for example the styrene/α-methyl styrene system[3]. The visco-elastic properties of these homogeneous block copolymers are amenable to theoretical treatment by the bead-and-spring model enunciated by Rouse[6], Bueche[7], and Zimm[8] (the RBZ model). In this paper, we shall discuss the molecular theory of visco-elasticity for homogeneous block copolymers[9-13]. The results of the calculations are compared with the experimental data on the diblock and triblock copolymers of styrene and α-methyl styrene[13,14].

THEORY

The RBZ model represents the polymer molecule by re-placing the N submolecules with N+1 beads held together with N entropy springs. When the polymer coil is disturbed by a velocity gradient, the springs are stretched. The restoring force of these entropy springs is proportional to displacement, the spring constant being given by $3kT/b^2$ where b^2 is the average square end-to-end distance of the submolecule. As the beads move through the medium, a viscous drag is exerted on them whose magnitude is determined by the friction coefficient

f. As the flow ceases, the recovery of the polymer chain is effected without acceleration, so that the viscous and the elastic forces are exactly equal to each other.

For homopolymers, all of the beads in the model have identical spring constants and frictional coefficients. In the case of block copolymers, both of these parameters are expected to be different for different blocks in the polymer. For example, the equations of motion for an SAS triblock copolymer can be written as[9]:

$$\dot{\underline{x}} \;=\; -\sigma_S \; \underline{D}^{-1} \; \underline{Z} \; \underline{x} \quad \cdot \tag{1}$$

In eq. 1, $\underline{x}$ and $\dot{\underline{x}}$ are column vectors of bead positions and velocities respectively, $\underline{Z}$ is the nearest neighbor matrix, and $\sigma_S = 3kT/b_S^2 f_S$ where k is Boltzmann constant, T is the absolute temperature, b_S^2 is the mean square end-to-end distance and f_S is frictional coefficient. $\underline{D}^{-1}$ is the inverse of the following matrix

$$\underline{D} \;=\; \begin{bmatrix} 1_{1_1} & & & \bigcirc \\ & \ddots & \\ & & \delta_A \delta_A \\ & & & \ddots \\ \bigcirc & & & 1_{1_1} \end{bmatrix} \tag{2}$$

where

$$\delta_A \;=\; b_A^2 f_A / b_S^2 f_S \;=\; a_A^2 m_A^2 \zeta_A / a_S^2 m_S^2 \zeta_S \tag{3}$$

In eq. 3, m is the number of monomer units per submolecule,
a is the characteristic length, ζ is the monomeric friction
coefficient, and $b^2 = ma^2$. Subscripts A and S refer to
A-blocks and S-blocks respectively.

To solve eq. 3, we define a new set of coordinates
$\underline{r}$ related to $\underline{x}$ through

$$\underline{r} = \underline{A} \; \underline{x}, \tag{4}$$

where the $\underline{A}$ matrix is defined by $\underline{Z} = \underline{A}^T \underline{A}$. Operating on both
sides of eq. 1 with $\underline{A}$, we get

$$\dot{\underline{r}} = \sigma_A \underline{A} \; \underline{D}^{-1} \; \underline{A}^T \; \underline{A} \; \underline{x} \tag{5}$$

$$= -\sigma_A \; \underline{S} \; \underline{r} ,$$

where

$$\underline{S} = \underline{A} \; \underline{D}^{-1} \; \underline{A}^T \tag{6}$$

is a symmetrical tridiagonal NxN matrix which differs from
the well known Rouse matrix[6] ($\underline{R} = \underline{A} \; \underline{A}^T$) by the extra operation
$\underline{D}^{-1}$. For a homopolymer, all of the elements in our $\underline{D}$ matrix
are unity, and the $\underline{S}$ matrix is reduced to the $\underline{R}$ matrix.

The eigenvalue spectrum (λ_p's) of the $\underline{S}$ matrix is
readily obtained by numerical   methods on a computer[9]. In
order that the results are not functions of the matrix sizes
(number of beads), we use the following expression in computing
from the eigenvalues the normalized retardation times:

$$\tau_p(\text{normalized}) = 1/(N + 1)^2 \; \lambda_p \tag{7}$$

The model is readily adaptable to calculate the relaxation spectrum for any block configuration. The only change required is to make appropriate modifications of the $\underline{D}$ matrix. For instance, the $\underline{D}$ matrix for a diblock copolymer is[14]:

$$
\underline{D} = \begin{bmatrix} 1 & & & & & \bigcirc \\ & 1 & & & & \\ & & \ddots & & & \\ & & & \delta_A & & \\ & & & & \delta_A & \\ \bigcirc & & & & & \end{bmatrix} \tag{8}
$$

The same computer routine can then be used to perform all the required calculations.

COMPARISON WITH EXPERIMENT

In order to compare with the experimental data on triblock and diblock copolymers of styrene and α-methylstyrene, we shall identify S-block with polystyrene and A-blocks with poly(α-methylstyrene). We further need literature values of ζ's and a's for the respective blocks. In their recent work Osaki and Schrag[15] have found that the number of monomer units is 11 for PS(m_S) and 16 for PαMS(m_A).   On the basis of this information, we shall assume $m_A/m_S = 1.4$. In addition it has been reported that the characteristic length for PS(a_S)[16] is 7.4×10^{-8}cm, while for PαMS[17] $a_A = 8.0 \times 10^{-8}$ cm. The monomeric friction coefficients in eq. 3 are $\zeta_S = 1.15 \times 10^2$ and $\zeta_A = 2.08 \times 10^4$ dynes-sec/cm at their respective glass

transition temperatures (100°C and 167°C). The glass transition temperature is chosen as the reference state for comparing the monomeric friction coefficients because it is perferable to compare the ζ's at equivalent states of molecular motion as would be the case in a homogeneous copolymer. Using these values in eq. 3, we find[13] that

$\delta_A = 423$.

A matrix with 140 beads was used to compute the maximum ralexation time for 100% S beads. In calculating τ_M for the copolymers the molecular weight must remain fixed for a meaningful comparison. For simplicity the monomer molecular weight of styrene will be set to equal to that of α-MS. Thus

$$N_S + N_A \left(\frac{m_A}{m_S} \right) = 140 \tag{9}$$

where N_A and N_S are the number of PS and PαMS beads. Therefore the total number of beads in the chain ($N_A + N_S$) will decrease as the weight percent of α-MS increases.

$$\text{wt. } \% \ \alpha\text{-MS} = N_A m_A / (N_S m_S + N_A m_A) \tag{10}$$

The computed maximum relaxation times are given in Table 1. They are reduced by the maximum relaxation computed for PS (τ_m^o) for ease of comparison.

In order to compare with the theoretical results, block copolymers of styrene (S) and α-methylstyrene (A) were chosen for experimentation. Five triblock copolymers of poly(styrene-

b-α-methylstyrene-b-styrene) or SAS are synthesized by the

anionic technique[13]. In addition, one each of poly(α-methyl-

styrene-b-styrene-b-α-methylstryene)[13] or ASA, and poly-

(α-methylstyrene-b-styrene)[14], or AS, were used. Stress

relaxation techniques were used to generate viscoelastic

master curves by the Time-Temperature Superposition Princi-

ciple[13,14]. Distribution of relaxation times can be readily

computed from the master curves by well known methods[16]. One

such example for the SA block polymer[14] is shown in Fig. 1.

To assure the homogeneous nature of these block copolymers,

dynamic mechanical experiments were carried out. If the samples

indeed show no microphase separation, then only one primary

glass transition will be observed. A representative curve for

SA sample[4] is shown in Fig. 2. Here we see that there is only

one loss tangent peak rather than two. Similar data have been

reported for the other block copolymers[13,14]. Fig. 2 also

shows the dynamic storage moduli data for the sample[4]. There

is a precipitous drop in the modulus near 135°C, indicating

the onset of the primary glass transition of the polymer.

From the distribution of relaxation times given in Fig. 1,

it is simple to compute the linear viscoelastic parameters[16].

We have taken advantage of this technique to calculate the G'

and tan δ for the AS block copolymer as a function of log time,

then using the WLF shift factor data to transform the abscissa

to temperature. The solid line shows in Fig. 2 that there

is good agreement with the dynamic mechanical data.

The experimental maximum relaxation times of the block

copolymers were determined from the viscoelastic master curves

by using Precedure X of Tobolsky and Murakami[18]. Because the maximum relaxation times are strong functions of temperature and molecular weight, these effects must be compensated for in order to make a valid comparison. We shall use $T_i + 29°C$ as the reference temperature and 1.2×10^5 as the reference molecular weight. The relationship $d \ln\tau_m/d \ln M_w = 3.4$ was used to extrapolate the maximum relaxation times to the reference molecular weight. These experimental values of τ_m are given in Table 1. The maximum relaxation times were again normalized by τ_m for pure polystyrene. Since literature values[18,19] for τ_m of pure polystyrene differ somewhat from each other, an average value of $\log \tau_m^o = 2.36$(seconds) was used. As seen in Table 1, most of the normalized experimental and computed maximum relaxation times are in reasonable agreement for the SAS, ASA and AS block copolymers. The samples showing significant discrepancies are SAS with 5% and 42% α-methylstyrene. However, we note that the value of τ_m for the only ASA value in the figure is substantially higher than that of the SAS of comparable composition, as predicted by the theory.

ACKNOWLEDGEMENT

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Table 1.   Comparison of Experimental and Theoretical
           Maximum Viscoelastic Relaxation Times for Block
           Copolymers of Styrene and α-Methylstyrene[13,14].

Sample	Wt% αMS	$\log (\tau_m/\tau_m^o)$	
		Expt'l	Theor.
SAS	5	0.50	0.05
	17	0.59	0.55
	34	1.01	1.10
	42	0.89	1.50
	65	1.76	1.90
ASA	73	2.26	2.30
AS	50	1.75	1.75

FIGURE CAPTIONS

Figure 1.   Distribution of relaxation times for poly-
(α-methylstyrene-b-styrene) calculated from
the viscoelastic master curve[14] by the second
approximation method[16].

Figure 2.   Dynamic mechanical data at approximately 1 Hz
as a function of temperature for poly(α-methyl-
styrene-b-styrene)[4].   Solid lines are curves
computed from the stress relaxation data[14] by
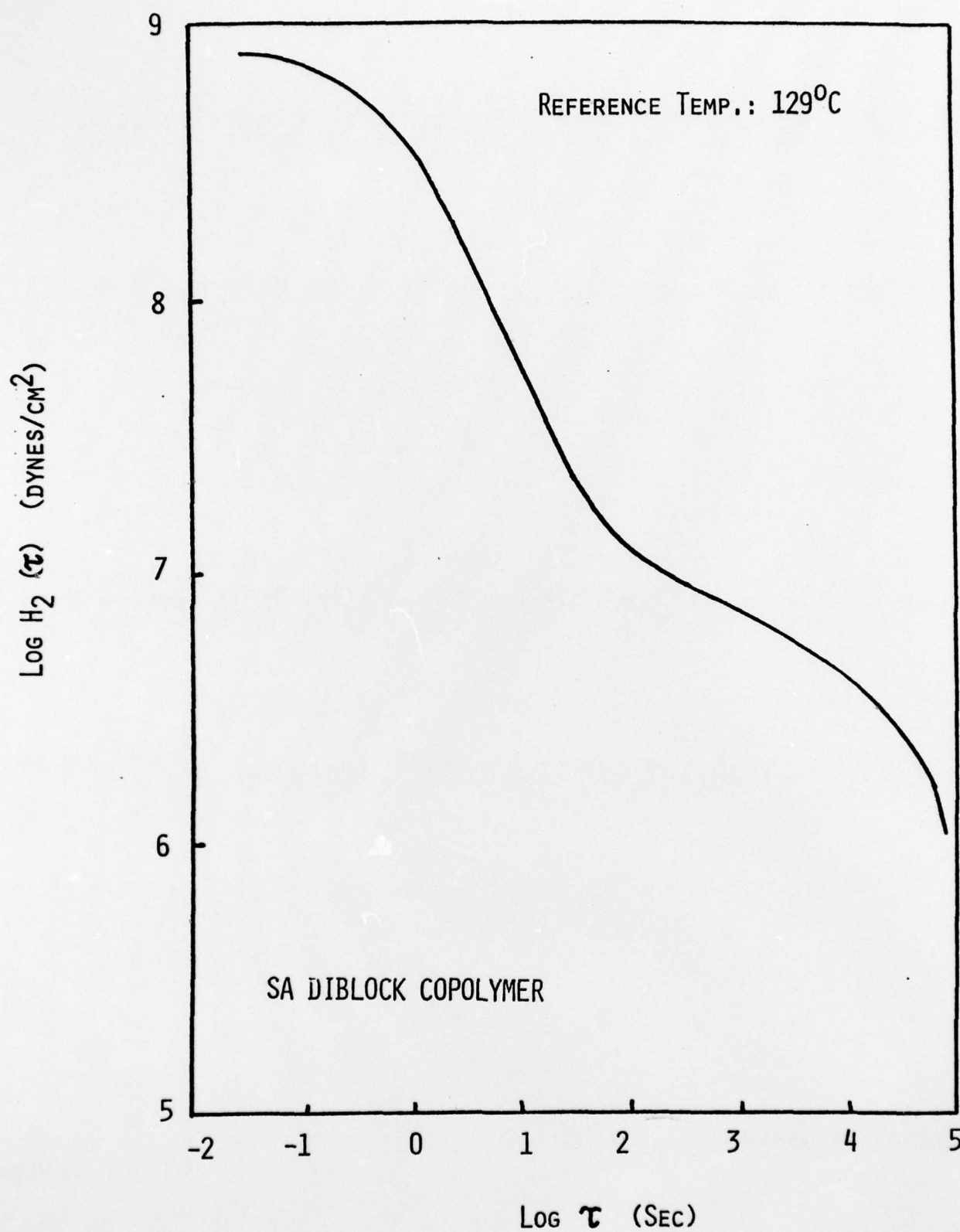using the distribution of relaxation times
given in Figure 1.

Fig. 1

REFERENCE TEMP.: 129°C

SA DIBLOCK COPOLYMER

Fig. 2

LOG G' (DYNES/CM^2)

SA DIBLOCK COPOLYMER

TEMPERATURE (°C)

LOG TAN δ